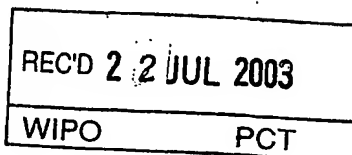




INVESTOR IN PEOPLE

The Patent Office
 Concept House
 Cardiff Road
 Newport
 South Wales
 NP10 8QQ



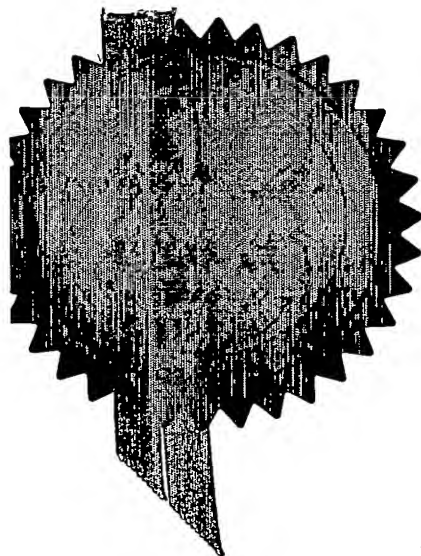
BEST AVAILABLE COPY

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

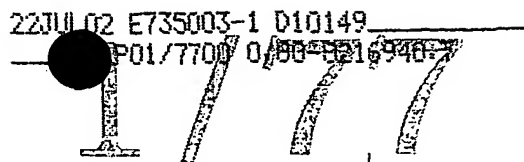
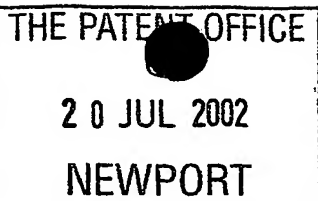


Signed

Dated

2 May 2003

PRIORITY DOCUMENT
 SUBMITTED OR TRANSMITTED IN
 COMPLIANCE WITH
 RULE 17.1(a) OR (b)



Request for grant of a patent

See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
South Wales
NP10 8QQ

1. Your reference	30060 P1			0216940.7
2. Patent application number (The Patent Office will fill in this part)	20 JUL 2002			
3. Full name, address and postcode of the or of each applicant (<u>underline all surnames</u>)	Givaudan SA Chemin de la Parfumerie 5 1214 Vernier Switzerland			
Patents ADP Number (if you know it)	8408031001			
If the applicant is a corporate body, give the country/state of its incorporation				
4. Title of the Invention	Improvements in or relating to organic compounds			
5. Name of your agent (if you have one)				
"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)	CIT Givaudan UK Ltd. Magna House 76-80 Church Street Staines, Middlesex TW18 4XR, England			
Patents ADP number (if you know it)	8408056001			
6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number	Country	Priority application number (if you know it)	Date of filing (day/month/year)	
7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application		Date of filing (day/month/year)	
8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if: a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body. See note (d)	yes			

Patents Form 1/77

1. Enter the number of sheets for any of the following items you are filing with this form.
Do not count copies of the same document

Continuation sheets of this form

Description 17

Claim(s) 2

Abstract 1

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination 1
and search (Patents Form 9/77)

Request for substantive examination
(Patents Form 10/77)

Any other documents
(please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature

Date 16/07/02

12. Name and daytime telephone number of person to contact in the United Kingdom
Colin Brown (office time) Tel. No: 01/784417721

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

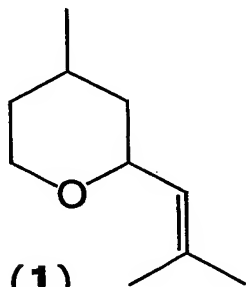
Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office

Improvements in or relating to organic compounds

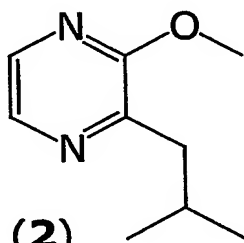
The invention is concerned with new fragrance ingredients, their manufacture and use in fragrance compositions, particularly in fine perfumery and cosmetics compositions.

During their investigations of the low-boiling constituents of Bulgarian rose oil in 1959, C. F. Seidel and M. Stoll (*Helv. Chim. Acta* 1959, 42, 1830) discovered an important trace constituent of green-metallic odor reminiscent of geranium oil and carrot leaves. They termed this new odorant rose oxide and later attributed it the structure 1 (C.F. Seidel, D. Felix, A. Eschenmoser, K. Biemann, E. Palluy, M. Stoll, *Helv. Chim. Acta* 1961, 44, 598). Though in substance the very powerful, green-metallic odor of rose oxide is rather unpleasant, today it is extensively used in many fragrances to provide diffusivity, lift and naturalness, especially in the top note of perfumes.



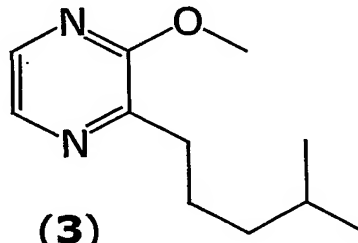
(1)

rose oxide



(2)

Galbazine



(3)

15

The methoxy pyrazines 2 and 3 represent another class of very powerful green odorants. 2 was first discovered by R. G. Buttery et al. in green bell pepper oil (R. G. Buttery, R. M. Seifert, R. E. Lundin, D. G. Guadagni, L. C. Ling, *Chem. Ind.* 1969, 490) and later also found in galbanum oil (A. F. Bramwell, J. W. K. Burrell, G. Riezebos, *Tetrahedron Lett.* 1969, 3215). It is reminiscent of peperoni, galbanum oil and green peas, and has been introduced into perfumery successfully as Galbazine®. Isohexyl methoxy pyrazine (3) with its more pleasant green, vegetable and hyacinth odor is also

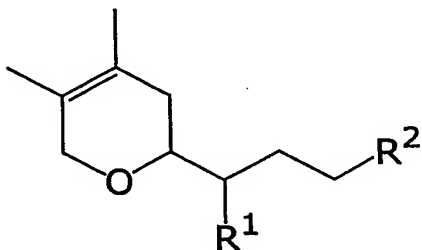
frequently used in perfumery, though in very low concentration due to its exceptional strength. Yet, even in high dilutions, all these pyrazines have harsh, unpleasant by-odors, which limit their use in perfumery.

Unfortunately, blending of the aforementioned materials has not lead
5 to any interesting odor tonalities without harsh, unpleasant or metallic-burnt aspects being noticeable.

Accordingly, there is a need to provide new ingredients to develop interesting odor tonalities that have proven inaccessible by simple blending of these known compounds.

10 Surprisingly, we have now found certain 3,6-dihydro-2H-pyrans, which possess the characteristic odor notes of methoxy pyrazines, but do not exhibit the harsh by-notes that prohibit the extensive use of these pyrazines in perfumery. Facettes of rose oxides are also present in these compounds leading to overall interesting, novel odor tonalities.

15 Therefore, the invention provides in a first aspect a compound of the general formula (I),



20 wherein $R^1 = H, CH_3 \text{ or } CH_2CH_3,$
 and $R^2 = H, CH_3, CH_2CH_3 \text{ or } CH_2CH_2CH_3,$ provided that
 when R^1 is H, R^2 is H.

25 The compounds of formula (I) may comprise more than one chiral centre and as such they may exist as a mixture of enantiomers and diastereomers, or they may be resolved as enantiomerically and

diastereomerically pure forms. However, resolving stereoisomers adds to the complexity of manufacture and purification of these compounds and so it is preferred to use a compound of formula (I) as a mixture of its stereoisomers simply for economic reasons. However, if it is desired to prepare pure stereoisomers, this may be achieved according to methodology known in the art.

Compounds of formula (I) may be prepared according to techniques known in the art using commercially available starting materials, or materials that can be easily prepared from known starting materials. The compounds may be prepared according to a retro-Diels-Alder reaction using 2,3-dimethyl-1,3-butadiene and an appropriately substituted aldehyde, for example butyraldehyde may be employed in the formation of compound (7) in Table 1. Reaction conditions for these Diels Alder reactions are more fully described in the Examples set forth below. The skilled person will appreciate that other compounds of the present invention may be prepared using an appropriately substituted aldehyde.

In another aspect of the present invention there is provided the use of a compound of the general formula (I) or mixtures thereof as a fragrance ingredient wherein,

$R^1 = H, CH_3 \text{ or } CH_2CH_3$, and
 $R^2 = H, CH_3, CH_2CH_3 \text{ or } CH_2CH_2CH_3$.

Compounds described hereinabove possess unique, character-donating aspects that that makes them suitable for a broad range of possible applications in perfumery. Furthermore, because the compounds do not possess the harsh unpleasant by-notes of the pyrazines exemplified by (2) and (3) above, they may confer a fresh green touch to virtually all kinds of perfume compositions, in virtually all kinds of applications from fine fragrances to cosmetics and detergents, e.g. in shampoos, skin-care products or soaps. Depending on the dosage, the effects can reach from providing more naturalness and character to building up hyazinth or petigrain or other green accords. The use is neither limited to any type of perfume nor to any special

olfactory directions, odorants or classes of substances. A few illustrative examples of classes of substances, which harmonize equally well are:

- 5 – ethereal oils and extracts, e.g. angelica oil, basilic oil, bergamot oil, carrot seed oil, citrus oils, coriander oil, galbanum oil, geranium oil, jasmin absolute, neroli oil, orris oil, petitgrain oil, rose oil, or violet leaf oil;
- 10 – alcohols, e.g. citronellol, cinnamic alcohol, dihydromyrcenol, Ebanol°, Florol°, geraniol, linalool, Mayol°, phenylethyl alcohol or terpineol ;
- 15 – aldehydes and ketones, e.g. decanal, *alpha*-hexylcinnamaldehyd, hydroxy-citronellal, isoeugenol, Iso E Super°, Isoraldeine°, Hedione°, methylionone or vanillin;
- 20 – ether and acetals, e.g. Ambrox°, 2-(1-ethoxyethoxy)ethyl benzene, geranyl methyl ether, Magnolan°, 2-(1-propoxyethoxy)ethyl benzene, or rose oxide (1).
- 25 – esters and lactones, e.g. benzyl acetat, benzyl salicylate, coumarin, γ -decalactone, ethylene brassylate, Thibetolide°, γ -undecalactone.
- 30 – heterocycles, e.g. indol, Galbazine (2) or 6-/8-isobutylchinoline.

Compounds of formula (I) that are particularly preferred for their fragrance properties are set forth in Table 1.

Table 1. Compounds of general formula (I) having R¹ and R² as indicated

Compound	R ¹	R ²
4	H	Methyl
5	H	Ethyl
6	H	Propyl
7	H	H
8	Ethyl	H
9	Methyl	H
10	Methyl	Methyl

Having regard to compounds in Table 1, compound 4, compound 5 and
5 compound 6 are known compounds, however, the olfactive properties of
these compounds have not been previously disclosed.

Compounds according to the formula (I) may be employed in any of
the fragrance compositions referred to above in widely varying amounts
having regard to the other fragrance ingredients employed and depending on
10 the fragrance accord that a perfumer is trying to achieve. Generally however,
one may employ about 0.01 to 1.0% by weight in fine fragrances and about
0.01 to 10% by weight in other perfumed products.

In addition to their admixture with other fragrance ingredients, the
compounds of formula (I) may be admixed with one or more excipients
15 conventionally used in conjunction with fragrances in fragrance
compositions, for example carrier materials, and other auxiliary agents
commonly used in the art such as solvents, preservatives, colourants and the
like.

The invention is now illustrated with reference to the following
20 examples.

Examples

4,5-Dimethyl-2-propyl-3,6-dihydro-2H-pyran (Compound 7):

2-Nitropropane (1.8 ml, 20 mmol) was added at 0 °C to a stirred suspension of aluminium trichloride (2.67 g, 20 mmol) in dichloromethane (50 ml). A solution of butanal (14.4 g, 200 mmol) in dichloromethane (30 ml) was added, followed by dropwise addition of 2,3-dimethyl-1,3-butadiene (24.6 g, 300 mmol) at 0 °C. After stirring for 3h at this temperature, and for 1h at ambient temperature, the reaction mixture was poured into water (400 ml) and the product extracted with pentane (3x 300 ml). The combined organic extracts were dried, concentrated in vacuo, and purified by silica-gel FC (pentane/MTBE, 99:1) to provide the title compound 7 (3.55 g, 12%).

Odor: green, spicy, rose oxide, vegetable. – IR (neat): ν = 1098 cm^{-1} (ν C–O–C), 1386 (δ CH₃), 1449 (δ CH₂). – ¹H-NMR (CDCl₃): δ = 0.93 (t, J = 7.0 Hz, 3H, 5'-H₃), 1.34–1.57 (m, 4H, 1'-H₂–2'-H₂), 1.53 / 1.63 (2s, 6H, 4-,5-Me), 1.80 (d, J = 16.5 Hz, 1H, 3-H_b), 1.93 (br. t, J = 16.5 Hz, 1H, 3-H_a), 3.47 (m, 1H, 2-H), 3.93 / 4.01 (2d, J = 15.5 Hz, 2H, 6-H₂). – ¹³C-NMR (CDCl₃): δ = 13.8 (q, 5-Me), 14.1 (q, C-3'), 18.3 (q, 4-Me), 18.6 (C-2'), 36.7 (t, C-3), 38.0 (t, C-1'), 69.8 (t, C-6), 73.9 (d, C-2), 123.5 / 124.3 (2s, C-4,-5). – MS (EI): m/z (%) = 41 (45) [C₃H₅⁺], 55 (55) [C₄H₇⁺], 67 (100) [C₅H₇⁺], 82 (99) [C₆H₁₀⁺], 111 (19) [M⁺–C₃H₇], 139 (21) [M⁺–CH₃], 154 (67) [M⁺].

2-(1-Ethylpropyl)-4,5-dimethyl-3,6-dihydro-2H-pyran (Compound 8):

2-Nitropropane (1.8 ml, 20 mmol) was added at –10 °C to a stirred suspension of aluminium trichloride (2.67 g, 20 mmol) in dichloromethane (80 ml). At this temperature, 2-ethylbutanal (20.0 g, 200 mmol) was added dropwise during 20 min, followed by 2,3-dimethyl-1,3-butadiene (24.6 g, 300 mmol) during 30 min. After further stirring at this temperature for 30 min, and for 1h at ambient temperature, the reaction mixture was poured into water (300 ml) and the product extracted with MTBE (3x 300 ml). The combined organic

extracts were dried, concentrated in vacuo, and purified by silica-gel FC (pentane/MTBE, 100:1, R_f = 0.47) to provide the title compound 8 (5.53 g, 15%).

Odor: green, carrot leaves, rose oxide, metallic, green peas, galbanum. – IR (neat): ν = 1099 cm^{-1} (ν C–O–C), 1384 (δ CH₃), 1461 (δ CH₂). – ¹H-NMR (CDCl₃): δ = 0.88 (t, J = 7.5 Hz, 6H, 3'-,2''-H₂), 1.53 / 1.64 (2s, 6H, 4-,5-Me), 1.19–1.50 (m, 5H, 1'-H, 2'-,1'''-H₂), 1.74 (br. d, J = 16.0 Hz, 1H, 3-H_b), 2.03 (br. t, J = 16.0, 1H, 3-H_a), 3.41 (m, 1H, 2-H), 3.93 / 3.99 (2d, J = 15.5 Hz, 2H, 6-H₂). – ¹³C-NMR (CDCl₃): δ = 11.2 / 11.3 (2q, C-3',-2''), 13.7 (q, 5-Me), 18.4 (q, 4-Me), 21.2 / 21.3 (2t, C-2',-1'''), 33.5 (t, C-3), 45.5 (d, C-1'), 70.1 (t, C-6), 75.8 (d, C-2), 123.8 / 124.4 (2s, C-4,-5). – MS (EI): m/z (%) = 41 (45) [C₃H₅⁺], 55 (54) [C₄H₇⁺], 67 (66) [C₅H₇⁺], 83 (100) [C₆H₁₁⁺], 111 (65) [M⁺–C₅H₁₁], 182 (28) [M⁺].

15 2-Butyl-4,5-dimethyl-3,6-dihydro-2H-pyran (Compound 4):

2-Nitropropane (1.8 ml, 20 mmol) was added at 0 °C to a stirred suspension of aluminium trichloride (2.67 g, 20 mmol) in dichloromethane (80 ml). Pentanal (17.2 g, 200 mmol) was added at –78 °C, followed by 2,3-dimethyl-
20 1,3-butadiene (24.6 g, 300 mmol). The cooling bath was removed and the reaction was stirred at room temperature for 3h. The mixture was then poured into water (400 ml), and the product extracted with pentane (3x 400 ml). The organic extracts were combined and dried, the solvent was evaporated in vacuo, and the resulting residue purified by distillation to
25 furnish at 34–38 °C / 0.05 mbar the title compound 4 (7.87 g, 12%).

Odor: green, spicy, rose oxide, hyacinth. – IR (neat): ν = 1100 cm^{-1} (ν C–O–C), 1387 (δ CH₃), 1450 (δ CH₂). – ¹H-NMR (CDCl₃): δ = 0.91 (t, J = 7.0 Hz, 3H, 5'-H₃), 1.30–1.58 (m, 6H, 1'-H₂–3'-H₂), 1.53 / 1.63 (2s, 6H, 4-,5-Me), 1.80 (d, J = 16.0 Hz, 1H, 3-H_b), 1.94 (br. t, J = 16.0 Hz, 1H, 3-H_a), 3.45 (m, 1H, 2-H), 3.93 / 4.01 (2d, J =
30

15.5 Hz, 2H, 6-H₂). – ¹³C-NMR (CDCl₃): δ = 13.8 (q, 5-Me), 14.0 (q, C-4'), 18.3 (q, 4-Me), 22.7 (t, C-3'), 27.7 (t, C-2'), 35.6 / 36.7 (t, C-3,-1'), 69.8 (t, C-6), 74.2 (d, C-2), 123.5 / 124.3 (2s, C-4,-5). – MS (EI): *m/z* (%) = 41 (36) [C₃H₅⁺], 55 (41) [C₄H₇⁺], 67 (79) [C₅H₇⁺], 82 (100) [C₆H₁₀⁺], 85 (58) [C₅H₉O⁺], 111 (20) [M⁺–C₄H₉], 153 (16) [M⁺–CH₃], 168 (54) [M⁺].

4,5-Dimethyl-2-pentyl-3,6-dihydro-2H-pyran (Compound 5):

10 2-Nitropropane (1.8 ml, 20 mmol) was added at –10 °C to a stirred suspension of aluminium trichloride (2.67 g, 20 mmol) in dichloromethane (80 ml). At this temperature, a solution of hexanal (20.0 g, 200 mmol) in dichloromethane (80 ml) was added within 15 min, followed by dropwise addition of 2,3-dimethyl-1,3-butadiene (24.6 g, 300 mmol) in a period of
15 another 15 min. After further stirring at 0 °C for 90 min, the cooling bath was removed, and another portion of 2,3-dimethyl-1,3-butadiene (24.6 g, 300 mmol) was added dropwise with stirring at room. Stirring was continued at ambient temperature for 14 h, prior to pouring the reaction mixture into water (400 ml) and extraction of the product with MTBE (3x 400 ml). The
20 combined organic extracts were dried, the solvent was removed under reduced pressure, and the resulting residue purified by distillation in vacuo to provide at 53–58 °C / 0.30–0.35 mbar the title compound 5 (5.41 g, 15%).

Odor: Strong, green peas, vegetable, isohexyl methoxy pyrazine, lily and
25 hyacinth. – IR (neat): ν = 1102 cm^{–1} (ν C–O–C), 1386 (δ CH₃), 1449 (δ CH₂), 1691 (ν C=C). – ¹H-NMR (CDCl₃): δ = 0.89 (t, *J* = 7.0 Hz, 3H, 5'-H₃), 1.27–1.69 (m, 8H, 1'-H₂–4'-H₂), 1.53 / 1.59 (2s, 6H, 4-,5-Me), 1.80 (d, *J* = 16.0 Hz, 1H, 3-H_b), 1.94 (br. t, *J* = 16.0 Hz, 1H, 3-H_a), 3.45 (m, 1H, 2-H), 3.93 / 4.01 (2d, *J* = 15.5 Hz, 2H, 6-H₂). –
13C-NMR (CDCl₃): δ = 13.8 (q, 5-Me), 14.0 (q, C-5'), 18.3 (q, 4-Me), 22.6 (t, C-4'),
30 25.1 (t, C-2'), 31.9 (t, C-3'), 35.8 / 36.7 (t, C-3,-1'), 69.8 (t, C-6), 74.2 (d, C-2), 123.5 /

124.3 (2s, C-4,-5). – MS (EI): m/z (%) = 41 (32) [$C_3H_5^+$], 55 (38) [$C_4H_7^+$], 67 (64) [$C_5H_7^+$], 82 (100) [$C_6H_{10}^+$], 111 (20) [$M^+ - C_5H_{11}$], 167 (11) [$M^+ - CH_3$], 182 (37) [M^+].

5

2-Hexyl-4,5-dimethyl-3,6-dihydro-2H-pyran (Compound 6):

2-Nitropropane (1.8 ml, 20 mmol) was added at -10°C to a stirred suspension of aluminium trichloride (2.67 g, 20 mmol) in dichloromethane (80 ml).
 10 Heptanal (22.8 g, 200 mmol) was added dropwise at this temperature during 15 min, followed by dropwise addition of 2,3-dimethyl-1,3-butadiene (24.6 g, 300 mmol) during 20 min. The reaction was stirred -10°C for 15 min., and at room temperature for 1h. Another portion of 2,3-dimethyl-1,3-butadiene (24.6 g, 300 mmol) was added during 20 min, and stirring was continued at
 15 room temperature for 15 h. The mixture was then poured into water (300 ml), and the product extracted with MTBE (3x 300 ml). The organic extracts were combined and dried, the solvent was evaporated in vacuo, and the resulting residue purified by FC (pentane/ether, 100:1) on silica gel to provide the title compound 6 (2.78 g, 7%).

20

Odor: Strong, green peas, parsley, vegetable, pyrazine, roots. – IR (neat): ν = 1104 cm^{-1} (ν C–O–C), 1456 (δ CH_2), 1386 (δ CH_3), 1693 (ν C=C). – $^1\text{H-NMR}$ (CDCl_3): δ = 0.88 (t, J = 7.0 Hz, 3H, 6'- H_3), 1.29–1.69 (m, 10H, 1'- H_2 –5'- H_2), 1.53 / 1.63 (2s, 6H, 4,5-Me), 1.80 (d, J = 16.0 Hz, 1H, 3- H_b), 1.94 (br. t, J = 16.0 Hz, 1H, 3- H_a), 3.45 (m, 1H, 2-H), 3.93 / 4.01 (2d, J = 16.0 Hz, 2H, 6- H_2). – $^{13}\text{C-NMR}$ (CDCl_3): δ = 13.8 (q, 5-Me), 14.1 (q, C-6'), 18.3 (q, 4-Me), 22.6 (t, C-5'), 25.4 (t, C-2'), 29.4 (t, C-3'), 31.8 (t, C-4'), 35.9 / 36.7 (t, C-3,-1'), 69.8 (t, C-6), 74.3 (d, C-2), 123.5 / 124.3 (2s, C-4,-5). – MS (EI): m/z (%) = 41 (24) [$C_3H_5^+$], 55 (29) [$C_4H_7^+$], 67 (51) [$C_5H_7^+$], 82 (100) [$C_6H_{10}^+$], 85 (52) [$C_6H_{13}^+$], 111 (21) [$M^+ - C_6H_{13}$], 181 (13) [25
 30 [$M^+ - \text{CH}_3$], 196 (37) [M^+].

4,5-Dimethyl-2-(1-methylpropyl)-3,6-dihydro-2H-pyran (Compound 9):

5 To a suspension of aluminum trichloride (2.67 g, 20 mmol) in dichloromethane (50 ml) was added 2-nitropropane (1.8 ml, 20 mmol) at 0 °C. At the same temperature, a solution of 2-methylbutanal (17.2 g, 200 mmol) and 2,3-dimethylbutadiene (24.6 g, 300 mmol) in dichloromethane (30 ml) was added dropwise with stirring, and stirring was continued at 0 °C for 30
 10 min. and at room temperature for 2 h, prior to the addition of another portion of 2,3-dimethylbutadiene (24.6 g, 300 mmol). After further stirring at room temperature for 15 h, the reaction mixture was poured into water (300 ml) and the product was extracted with MTBE (3x 300 ml). The combined organic extracts were dried and concentrated under reduced pressure. The resulting
 15 crude product was purified by distillation to provide at 90–92 °C / 20 mbar the title compound 9 (5.76 g, 17%).

Odor: Rose oxide, green, aromatic. – IR (neat): $\nu = 1099 \text{ cm}^{-1}$ ($\nu \text{ C-O-C}$), 1383 ($\delta \text{ CH}_3$), 1457 ($\delta \text{ CH}_2$). – $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.91 / 0.97$ (2d, $J = 7.0 \text{ Hz}$, 3H, 1'-Me),
 20 0.92 / 0.93 (2t, $J = 7.0 \text{ Hz}$, 3H, 4'-H₃), 1.15–1.64 (m, 3H, 1'-H, 2'-H₂), 1.56 / 1.67 (2s, 6H, 4,5-Me), 1.77 (2 br. d, $J = 16.0 \text{ Hz}$, 1H, 3-H_b), 2.05 / 2.08 (2 br. t, $J = 16.0 \text{ Hz}$, 1H, 3-H_a), 3.30 (m, 1H, 2-H), 3.97 / 4.03 (2d, $J = 15.5 \text{ Hz}$, 2H, 6-H₂). – $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 11.3 / 11.5$ (q, C-3'), 13.7 / 13.8 / 14.2 / 14.6 (4q, 5-Me, C-4'),
 25 18.4 / 18.5 (2q, 4-Me), 25.0 / 25.4 (2t, C-2'), 33.1 / 33.7 (2t, C-3), 39.2 / 39.3 (2d, C-1'), 70.1 / 70.2 (2t, C-6), 77.9 / 77.9 (2d, C-2), 123.7 / 123.8 / 124.4 / 124.4 (4s, C-4,-5). – MS (EI): m/z (%) = 41 (44) [C_3H_5^+], 55 (59) [C_4H_7^+], 67 (75) [C_5H_7^+], 83 (100) [$\text{C}_6\text{H}_{11}^+$], 111 (58) [$\text{M}^+ - \text{C}_4\text{H}_9$], 153 (2) [$\text{M}^+ - \text{CH}_3$], 168 (45) [M^+].

30 4,5-Dimethyl-2-(1-methylbutyl)-3,6-dihydro-2H-pyran (Compound 10):

2-Nitropropane (1.8 ml, 20 mmol) was added at -10°C to a stirred suspension of aluminium trichloride (2.67 g, 20 mmol) in dichloromethane (80 ml). At this temperature, 2-methylpentanal (20.0 g, 200 mmol) was added dropwise during 20 min, followed by 2,3-dimethyl-1,3-butadiene (24.6 g, 300 mmol) during 30 min. After further stirring at this temperature for 30 min, and for 1h at ambient temperature, the reaction mixture was poured into water (300 ml) and the product extracted with MTBE (3x 300 ml). The combined organic extracts were dried, concentrated in vacuo, and purified by silica-gel FC (pentane/MTBE, 100:1, $R_f = 0.21$) to provide the title compound 10 (7.43 g, 20%).

Odor: Green, vegetable, aromatic, tea-like. – IR (neat): $\nu = 1101\text{ cm}^{-1}$ ($\nu\text{ C-O-C}$), 1383 ($\delta\text{ CH}_3$), 1456 ($\delta\text{ CH}_2$). – $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.88 / 0.94$ (2d, $J = 7.0\text{ Hz}$, 3H, 1'-Me), 0.89 / 0.90 (2t, $J = 7.0\text{ Hz}$, 3H, 4'-H₃), 1.10–1.61 (m, 5H, 1'-H, 2'-,3'-H₂'), 1.52 / 1.64 (2s, 6H, 4,5-Me), 1.73 (br. d, $J = 16.5\text{ Hz}$, 1H, 3-H_b), 2.05 (m, 1H, 3-H_a), 3.26 (m, 1H, 2-H), 3.94 / 4.00 (2 br. d, $J = 15.5\text{ Hz}$, 2H, 6-H₂). – $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 13.8 / 14.3 / 14.7 / 15.1$ (4q, 5-Me, C-4'), 18.3 / 18.4 (2q, 4-Me), 20.1 / 20.2 (2t, C-2'), 33.0 / 33.6 (2t, C-3'), 34.6 / 35.0 (2t, C-3), 37.3 / 37.5 (2d, C-1'), 70.1 / 70.2 (2t, C-6), 78.1 / 78.2 (2d, C-2), 123.6 / 123.7 / 124.4 / 124.4 (4s, C-4,-5). – MS (EI): m/z (%) = 43 (44) [C_3H_7^+], 55 (55) [C_4H_7^+], 67 (67) [C_5H_7^+], 83 (100) [$\text{C}_6\text{H}_{11}^+$], 111 (63) [$\text{M}^+ - \text{C}_5\text{H}_{11}$], 167 (2) [$\text{M}^+ - \text{CH}_3$], 182 (30) [M^+].

Floral-green perfume oil for fabric softeners:

25

	<u>compound/ingredient</u>	<u>parts by weight 1/1150</u>
	1. Agrumex (<i>ortho-tert</i> -Butylcyclohexyl acetate)	5
	2. Aubepine (<i>para</i> -Methoxybenzaldehyde) / <i>para</i> -cresol	15
30	3. Benzyl acetate	25
	4. Benzyl salicylate	35

	5.	<i>para-tert</i> -Butylcyclohexyl acetate	106
	6.	Butyl hydroxy toluene	2
	7.	Cinnamic alcohol	5
	8.	Citronellol, extra quality	50
5	9.	Coumarine, pure, crystalline	10
	10.	Damascenone @ 1% in DPG	10
	11.	<i>alpha</i> -Damascone @ 10% in DPG	4
	12.	<i>gamma</i> -Decalactone	4
	13.	Decanal	4
10	14.	Dihydromyrcenol	40
	15.	DPG (Dipropylene glycol)	20
	16.	Ebanol (3-Methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol)	3
	17.	Ethyl vanillin	3
15	18.	Eugenol, pure @ 10% in DPG	10
	19.	Fixolide (6-Acetyl-1,1,2,4,4,7-hexamethyltetralin)	10
	20.	Galaxolide 50 PHT (4,6,6,7,8,8-Hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[g]benzopyran)	100
	21.	Gardenol (1-Phenylethyl acetate)	15
20	22.	Geraniol	40
	23.	<i>alpha</i> -Hexylcinnamaldehyde	90
	24.	6-/8-Isobutylquinoline @ 10% in DPG	5
	25.	Isoraldeine 70 (8-Methylionone)	50
	26.	Lilial (2-Methyl-3-(4- <i>tert</i> -butylphenyl)propanal)	80
25	27.	Linalool	80
	28.	Manzanate (Ethyl 2-methyl pentanoate) @ 10% in DPG	5
	29.	Mayol (<i>para</i> -Isopropylcyclohexylmethanol)	2
	30.	Menthone @ 10% in DPG	5
	31.	2-Methyldecanal @ 10% in DPG	3
30	32.	6-Methylhept-5-en-2-one @ 10% in DPG	10
	33.	Methyl isoeugenol	5

	34.	Methyl salicylate @ 10% in DPG	5
	35.	Nerol, extra quality	10
	36.	Okoumal (2,4-Dimethyl-2-(1,1,4,4-tetramethyl- tetralin-6-yl)-1,3-dioxolane)	15
5	37.	2-Phenylethanol	25
	38.	Strawberry pure (Ethyl 3-methyl-3-phenyl- glycidate) @ 10% in DPG	10
	39.	Terpenyl acetate	40
	40.	Terpineol, pure	70
10	41.	<i>gamma</i> -Undecalactone	4
	42.	Undecanal	40
	43.	10-Undecenal @ 10% in DPG	20
	44.	Verdyl acetate	30
	45.	Veloutone (2,2,5-Trimethyl-5-pentylcyclo- pentanone) @ 10% in DPG	10
15	46.	Ylang ylang oil	15
	47.	Compound 5 @ 10% in DPG	5
			<hr/>
			<u>1150</u>

20

Compound 5 conveys to this perfume freshness and lift, and in particular
petigrain-type aspects. It combines very well with the aldehydes, and turns
the top note of the fragrance oil more eau de cologne-like; thereby, 5
attenuates the functional aspects of the fragrance and the fabric softener
25 becomes overall more sophisticated, more refined.

Floral-marine fragrance for soap:

30 compound/ingredient parts by weight 1/820

	1.	Agrumex (2- <i>tert</i> -Butylcyclohexyl acetate)	30
	2.	Ambrofix (3-Methyldodechydro-6,6-9a-oxidotetranorlabdane) @ 10% in DEP	2
	3.	Aubepine (<i>para</i> -Methoxybenzaldehyde)	2
5		/ <i>para</i> -cresol @ 10% in DPG	80
	4.	Bergamot Givco 104	30
	5.	<i>iso</i> -Butyl benzoate	2
	6.	Cassis Base 345-F CS	
	7.	Cetone V (1-(2,6,6-Trimethyl-2-cyclohexen-1-yl)-hepta-1,6-dien-3-one)	2
10			5
	8.	Citral	10
	9.	Citron Ess Reconst 1385	1
	10.	Citronellyl nitrile	20
	11.	<i>beta</i> -Damascone @ 1% in DPG	4
15	12.	2,4-Dimethyl-3-cyclohexenecarboxaldehyde	83
	13.	DPG (Dipropylene glycol)	
	14.	Floralozone (<i>alpha, alpha</i> -Dimethyl-4-ethylbenzenepropanal)	5
	15.	Galaxolide 50 PHT (4,6,6,7,8,8-Hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[g]benzopyran)	30
20			5
	16.	Geraniol, extra quality	100
	17.	Hedione	5
	18.	<i>cis</i> -3-Hexenol @ 10% in DPG	5
	19.	<i>cis</i> -3-Hexenyl acetate @ 10% in DPG	5
25	20.	<i>cis</i> -3-Hexenyl butyrate @ 10% in DPG	10
	21.	<i>cis</i> -3-Hexenyl hexenoate @ 10% in triethyl citrate	100
	22.	<i>alpha</i> -Hexylcinnamaldehyde	15
	23.	<i>beta</i> -Ionone	2
	24.	<i>cis</i> -Jasmone	50
30	25.	Linalool	3
	26.	Mandarinal Base (Firmenich)	

	27.	Methyl 2-nonynoate @ 1% in DPG	5
	28.	Nerolidol	100
	29.	Neroli oil	2
	30.	Nutmeg (mace) oil @ 10 % in DPG	2
5	31.	Phenylethyl phenylacetate	3
	32.	Terpenyl Acetate	50
	33.	Terpineol, pure	20
	34.	Terpinolene	10
	35.	<i>gamma</i> -Undecalactone	2
10	36.	Compound 5 @ 10% in DPG	20

820

Compound 5 harmoniously combines the hesperidic, floral-marine and green notes of the fragrance; thereby, it rounds off the composition and increases its radiance. In addition, it introduces naturalness and increases the character of that fragrance. At this relatively high dosage, 5 brings as well facettes of petitgrain oil and jasmone in; overall, 5 conveys to the fragrance its unique texture, its fresh and hygienic but also soft and caressing character.

20

Essai for a male fine fragrance:

	<u>compound/ingredient</u>	<u>parts by weight 1/1000</u>
25	1. Ambrein, pure Base (Biolande)	2
	2. Anise oil	2
	3. Artemisia (Armoise) oil	3
	4. Bergamotte Givco 104	80
30	5. Benzyl salicylate	50
	6. Birch Leaf Givco 166	4

	7.	Bornyl acetate	5
	8.	Coumarine, pure	5
	9.	Cyclal C (2,4-Dimethyl-3-cyclohexene carboxaldehyde)	1
	10.	<i>delta</i> -Damascone	1
5	11.	Dihydromyrcenol	120
	12.	DPG (Dipropylene glycol)	95
	13.	Evernyl (Methyl 3,6-dimethylresorcylate)	8
	14.	Fir balsam resinoide	2
10	15.	Galaxolide 50 PHT (4,6,6,7,8,8-Hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[g]benzopyran)	180
	16.	Galbanone 10 (1-(5,5-Dimethyl-1-cyclohexen-1-yl)-4-penten-1-one)	5
	16.	Gardenol (1-Phenylethyl acetate)	2
	17.	Geranium oil	8
15	18.	Hedione	150
	19.	Iso E Super	160
	20.	Kephalis (4-(1-Ethoxyethenyl)-3,3,5,5-tetramethylcyclohexanone)	15
	21.	Lavandin Grosso oil	3
20	22.	Linalool	40
	23.	Melonal (2,6-Dimethylhept-5-enal) @ 10% in DPG	1
	24.	Nutmeg (mace) oil	5
	25.	Patchouli oil (iron free)	8
	26.	Radjanol	40
25	36.	Compound 5	5
			<hr/>
			<u>1000</u>

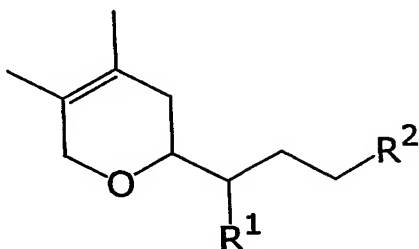
Compound 5 conveys to this male fine fragrance essai it's fresh facet: A green
 30 and invigorating botanical freshness, clean, clear and compelling. It enriches
 the classical top of this modern fougere by new aspects, increases radiance

30060P1

and diffusion, and harmonizes and stages the spicy accord of anise, artemisia and nutmeg oils. In result, this masculine scent acquires a herbal crispness that doesn't disturb the mysterious sensuality of the woody-musky-mossy-coumarine fond, but instead accentuates it.

Claims

1. A compound of the general formula (I)



or mixtures thereof,

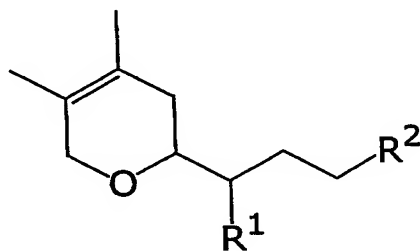
wherein,

$R^1 = H, CH_3$ or CH_2CH_3 ,

$R^2 = H, CH_3, CH_2CH_3$ or $CH_2CH_2CH_3$,

provided that when R^1 is H, R^2 is H.

2. A compound according to claim 1 selected from the group consisting of 2-(1-ethylpropyl)-4,5-dimethyl-3,6-dihydro-2H-pyran; 4,5-dimethyl-2-propyl-3,6-dihydro-2H-pyran; 4,5-dimethyl-2-(1-methylpropyl)-3,6-dihydro-2H-pyran; 4,5-dimethyl-2-(1-methylbutyl)-3,6-dihydro-2H-pyran; or mixtures thereof.
3. The use of a compound of the formula (I)



wherein,

R^1 is H, CH_3 or CH_2CH_3 , and

R^2 is H, $CH_3, CH_2CH_3, CH_2CH_2CH_3$

as a fragrance ingredient.

4. Use according to claim 3 wherein the compound is selected from the group consisting of 2-butyl-4,5-dimethyl-3,6-dihydro-2H-pyran; 4,5-dimethyl-2-pentyl-3,6-dihydro-2H-pyran; 2-(1-ethylpropyl)-4,5-dimethyl-3,6-dihydro-2H-pyran; 2-hexyl-4,5-dimethyl-3,6-dihydro-2H-pyran; 4,5-dimethyl-2-propyl-3,6-dihydro-2H-pyran; 4,5-dimethyl-2-(1-methylpropyl)-3,6-dihydro-2H-pyran; 4,5-dimethyl-2-(1-methylbutyl)-3,6-dihydro-2H-pyran; or mixtures thereof.
5. A fragrance composition comprising a compound as defined in any of the claims 3 or 4, or mixtures thereof.

Abstract

Disclosed are 2,4,5-trialkyl-substituted 3,6-dihydro-2H-pyrans that are useful as fragrance ingredients, particularly in fine fragrances and functional perfumery.